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Six New Three-Dimensional 3-Connected Nets $4.n^2$

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Abstract

Six new 3D 3-connected nets $4.n^2$ are described. These bring to seventeen the number of known 'Archimedean' 3D 3-connected nets, that is, nets which contain shortest circuits of more than one kind and have a configuration in which all points are symmetrically equivalent.

Apart from their obvious intrinsic interest, periodic networks of points that extend indefinitely in three dimensions are of importance in crystallography and structural chemistry as the basic frameworks underlying the structures of many crystals. If each point is joined to p others (p-connected net) the minimal value of p is 3 if a 3D network is to be formed. A net is described in terms of the shortest paths starting from a point along one link and returning to the point along another link. In a 3-connected net there are three ways of selecting two of the three links meeting at any point, and therefore three circuits (of n_1, n_2, and n_3 points) must be specified. The 3D 3-connected nets which are simplest from the topological standpoint are those in which all the shortest circuits are n-gons; these are the n^3 or $(n,3)$ nets – *uniform* nets. Uniform nets are known in which n is equal to 7, 8, 9, 10, or 12 (Wells, 1977, pp. 33–73). They are the 3D homologues of the 3-connected polyhedra $n = 3$, 4, and 5, and the 2D net $n = 6$. The (topological) symbol n^3 does not define the symmetry of the polyhedron or net. All the systems 3^3, 4^3, 5^3, and 6^3 have configurations in which all the points are symmetrically equivalent, that is, they may be described by a set of equivalent positions of a point group or plane group. The most symmetrical forms are the regular tetrahedron, cube, and regular pentagonal dodecahedron, and the regular hexagon net. Of the 30 known uniform 3D 3-connected nets only 7 have a configuration in which all points are symmetrically equivalent, that is, are described by a set of equivalent positions of one of the 230 space groups; these are two 8^3 nets, four 10^3 nets, and one 12^3 net.

The next group of 3D 3-connected nets comprises those in which the shortest circuits are of two or more kinds. Here also we may distinguish as a special set those which have a configuration in which all points are symmetrically equivalent. By analogy with the 3-connected Archimedian solids (and prisms), which have this property, we call these the Archimedean 3D 3-connected nets. Eleven such nets have been described (Wells, 1979, p. 10): 3.20^2, $4.6.8$, $4.8.10$ (two), 4.12^2 (two), 4.14^2, 6.8^2, 6.10^2, $8^2.10$, and 8.10^2. They were derived by replacing the points of appropriate p-connected nets by 3-, 4-, 6-, or 8-gons. A further

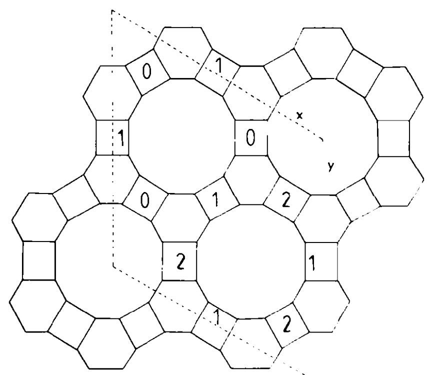

Fig. 1. The net 4.12^2-*b*. Numerals indicate the heights of 4-gons as multiples of $c/3$.

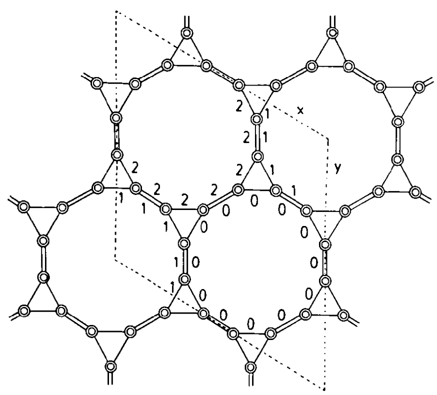

Fig. 2. The net 4.12^2-*c*. Numerals indicate the heights of *links* as multiples of $c/3$. The broken lines enclose the base of the hexagonal cell.

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six Archimedean nets have now been found, all of the type $4.n^2$. Projections of the new nets are shown in Figs. 1–6, where for simplicity we show the heights of *links* which lie in planes parallel to that of the projection rather than the heights of all the points. Since the discovery of these nets has necessitated the relabelling of two nets (4.12^2-*b* is now 4.12^2-*e*, and 4.14^2 becomes 4.14^2-*a*) we list all the known $4.n^2$ nets in Table 1.

There are two pairs of closely related nets. In the two nets which project as the plane net 4.6.12 (Figs. 1 and 5) the 4-gons are horizontal, and the space groups are $R\bar{3}m$ and $P6_222$. In the nets (Figs. 2 and 3) which project as 3.12^2 the 4-gons are perpendicular to the plane of projection, and the space groups are also $R\bar{3}m$ and $P6_222$. In all four nets $Z_t = 12$; the hexagonal cells (broken lines in Figs. 1 and 2) of the rhombohedral nets contain 36 points. It is interesting that the general position 12(*k*) serves for three of the new nets, the projections corresponding to the following values of the parameters *x*, *y*, and *z*:

	x	y	z
4.12^2-*d*	0.58	0.16	$\frac{1}{3}$
4.14^2-*c*	0.45	0.14	0
4.16^2	$\frac{1}{3}$	0	$\frac{1}{3}$.

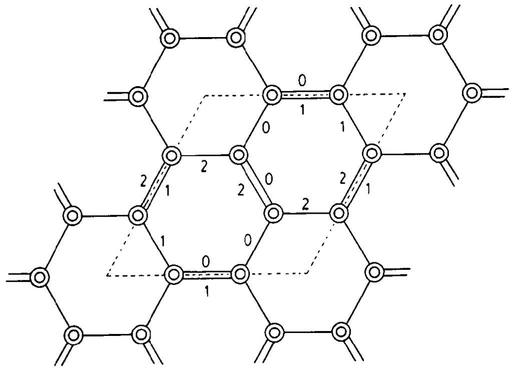

Fig. 6. The net 4.16^2. Numerals indicate the heights of links as multiples of $c/3$.

Table 1. *Archimedean 3D 3-connected nets* $4.n^2$

Net	Z_t	Space group	Equivalent position	Figure
4.12^2-*a*	12	$Im3m$	24(*g*)	
-*b*	12	$R\bar{3}m$	12(*i*)	1
-*c*	12	$R\bar{3}m$	12(*i*)	2
-*d*	12	$P6_222$	12(*k*)	3
-*e*	24	$Im3m$	48(*j*)	
4.14^2-*a*	8	$I4_1/amd$	16(*h*)	
-*b*	8	$I4_122$	16(*g*)	4
-*c*	12	$P6_222$	12(*k*)	5
4.16^2	12	$P6_222$	12(*k*)	6

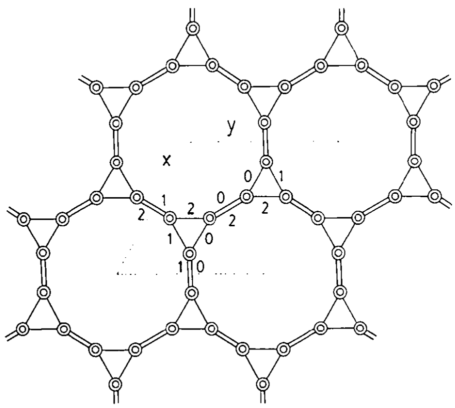

Fig. 3. The net 4.12^2-*d*. Numerals indicate the heights of links as multiples of $c/3$.

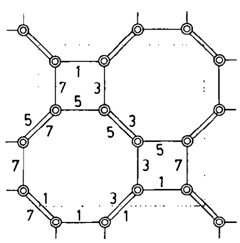

Fig. 4. The net 4.14^2-*b*. Numerals indicate the heights of links as multiples of $c/8$.

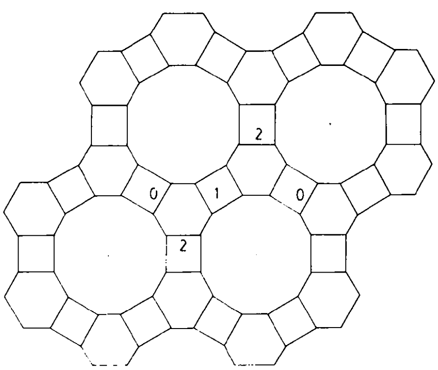

Fig. 5. The net 4.14^2-*c*. Numerals indicate the heights of 4-gons as multiples of $c/3$.

The net of Fig. 4, 4.14^2-*b*, is related in a simple way to 4.14^2-*a*, for both result from replacing the points of the diamond net by squares. In the configuration of 4.14^2-*a* illustrated in Fig. 2.8 (Wells, 1979) the planes of all the squares are perpendicular to the *c* axis, whereas in the configuration of 4.14^2-*b* of Fig. 4 successive squares in the *c*-axis direction are related by a 4_1 axis and lie in perpendicular planes. The diamond net is referable to a b.c. tetragonal cell containing four points; these two 4.14^2 nets are accordingly referable to b.c. tetragonal cells containing 16 points, with the space groups $I4_1/amd$ and $I4_122$ respectively. Since there are four variable parameters in 4.14^2-*b* ($c:a$, x, y, and z) there is no unique configuration; one with square 4-rings and all links of equal length has $x = y = 0{\cdot}104$ $\{$or $1/[4(1+\sqrt{2})]\}$, $z = \frac{1}{8}$, and $c:a = 1{\cdot}172$ [or $4/(2+\sqrt{2})$].

A structure based on a 3-connected net may be formed from any units which can be connected to three others, for example, tetrahedral AX_4 groups sharing three vertices or an edge and two vertices, or from octahedral AX_6 groups sharing three vertices, three edges, or other combination (totalling three) of vertices, edges, and faces. It might therefore be expected that such structures, particularly those built from octahedra, would provide many examples of 3-connected nets. A preliminary (unpublished) survey of octahedral AX_n and A_2X_n structures has revealed a considerable number of structures based on uniform and Archimedean 3-connected nets, including:

8^3-a:A_2X_7		6.10^2	A_2X_9,AX_4,A_2X_7
10^3-a:A_2X_7,AX_3		4.14^2-a	A_2X_9
10^3-b:A_2X_9,AX_4,A_2X_7,AX_3		4.14^2-b	AX_4
10^3-c:A_2X_9,AX_3,A_2X_7		$4.8.10$-a	AX_4.

However, no examples of any of these structures appear to be known; indeed, very few examples of structures of any kind based on Archimedean 3-connected nets are known (Wells, 1979, p. 15). It was the study of these octahedral structures that led to the derivation of the net 4.14^2-b, and this in turn suggested the nets of Figs. 2, 3, 4, and 6, in all of which the 4-gon circuits are perpendicular to the plane of projection and are shown as double lines. The net of Fig. 6 is of special interest as the only example at present known of a net 4.16^2; it continues the series which starts with the cube (4.4^2), truncated octahedron (4.6^2), plane net (4.8^2), double layer (4.10^2), and the 3D nets 4.12^2 and 4.14^2.

References

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SHORT COMMUICATION

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A note on the structure of $TiMnSi_2$ and the tetrahedrally close-packed 'pentagon–sigma' structure. By

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Abstract

The hypothetical tetrahedrally close-packed (t.c.p.) structure, which is a pentagon–triangle analogue of the hexagon–triangle σ phase, mentioned by Steinmetz, Venturini, Roques, Engel, Chabot & Parthé in their paper on the structure of $TiMnSi_2$ [*Acta Cryst.* (1982), B**38**, 2103–2108], has actually been found to exist in the W–Fe–Si system at approximate composition W_2FeSi by Kripyakevich & Yarmolyuk [*Dopov. Akad. Nauk. Ukr. RSR Ser. A* (1974), **36**, 460–463]. This 'pentagon–sigma' structure is one of four t.c.p. structures of composition R_6X_7 [R represents atoms with coordination number (CN) > 12, and X atoms with CN = 12]. The other structures are the M phase, the μ phase, and a hypothetical structure which has a projection almost identical to the projection of the hypothetical structure given in Fig. 3(b) of Steinmetz *et al.* (1982).

Steinmetz *et al.* (1982) observe that the c projection of $TiMnSi_2$ and $TiFeSi_2$ resembles closely the projection of a pentagon–triangle analogue, given in Fig. 6(b) in Shoemaker & Shoemaker (1969), of the hexagon–triangle σ phase. This 'pentagon–sigma' structure has actually been found to occur in the W–Fe–Si system [composition $W_6(Fe_{0.465}Si_{0.465}W_{0.07})_7$] by Kripyakevich & Yarmolyuk (1974). The space groups for $TiMnSi_2$ and the 'pentagon–sigma' structures are the same ($Pbam$, a and b interchanged, c approximately doubled in $TiMnSi_2$).

Although the c projections of the $TiMnSi_2$ and the 'pentagon–sigma' structures are almost identical, Steinmetz *et al.* (1982) point out that the structures are actually quite different: $TiMnSi_2$ has three secondary layers for four main layers, whereas the tetrahedrally close-packed (t.c.p.) structure has an equal number of secondary and main layers. The $TiMnSi_2$ structure contains octahedra of Si atoms (surrounding metal atoms), whereas the 'pentagon–sigma' structure has only possible Si–Si contacts through sites of mixed W, Fe, Si or Fe, Si occupancy. With 25 at.% Si 'W_2FeSi' is at the upper limit of Si content of t.c.p. structures described before.

The 'pentagon–sigma' structure was first proposed as a hypothetical structure by Frank & Kasper (1959) as entry 8 in their Table 3. They also proposed a hypothetical structure (entry 9 in the same table), which is the all-pentagon analogue of the pentagon–hexagon structure of the P phase. That hypothetical structure was later found to occur as the M phase in the Nb–Ni–Al system ($Nb_{48}Ni_{39}Al_{13}$, Shoemaker & Shoemaker, 1967). The 'pentagon–sigma' and the M phase are very similar to the t.c.p. μ phase (W_6Fe_7, Arnfelt & Westgren, 1935). The formula for all three phases may be written as R_6X_7, where R represents atoms with CN > 12, and X atoms with CN = 12 (Yarmolyuk & Kripyakevich,

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